(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 114 087**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **84300015.9**

(22) Date of filing: **03.01.84**

(51) Int. Cl.³: **C 23 F 7/08**, C 23 F 7/10, C 23 F 7/14, B 01 J 19/10

(30) Priority: **03.01.83 US 455296**
28.12.83 US 564635

(43) Date of publication of application: **25.07.84**
Bulletin 84/30

(84) Designated Contracting States: **BE DE FR GB IT NL SE**

(71) Applicant: **DETREX CHEMICAL INDUSTRIES, INC.,**
4000 Town Center Suite 1100, Southfield
Michigan 48075 (US)

(72) Inventor: **Otrhalek, Joseph V., 15693 Andover Drive,**
Dearborn Michigan 48120 (US)
Inventor: **Gerard, Donald Ray, 1012 Boone Court,**
Bowling Green Kentucky 42101 (US)

(74) Representative: **Carpmael, John William Maurice et al,**
CARPMAELS & RANSFORD 43 Bloomsbury Square,
London, WC1A 2RA (GB)

(54) **Zinc phosphate coated metal and process of producing same.**

(57) A method for forming conversion coating on metallic surfaces using an aqueous zinc phosphate immersion bath within which there is positioned a source of ultrasonic energy and the coated metallic object produced in carrying out the process in a controlled ultrasonic power environment.

EP 0 114 087 A1

For many years it has been known that aqueous zinc phosphate coatings when applied to metallic surfaces such as steel, galvanized iron and aluminium form conversion coatings which provide corrosion resistant properties to such metallic surfaces and likewise provide a surface to which siccative coatings such as paint will adhere. However, in preparing conversion coatings for a paint application, attempts to apply such conversion by immersion of the metal surfaces in a zinc phosphate bath have not been satisfactory due to the tendency under such conditions to form heavy, coarse coatings. Consequently, the art has turned to the use of spray processes to obtain finer coatings. Such spray processes have the disadvantage of a lesser penetration of crevices and inaccessible areas as compared to immersion processes but the coatings thus obtained are noticeably finer although still in need of improvement, particularly as to corrosion resistance. Another disadvantage of the processes of the art is the difficulty in coating the areas of steel surfaces upon which there lies carbon residue. Such areas of carbon residue on steel surfaces are common occurrences.

When used as a base for paint, the process of the present invention provides a fine-grained smooth, uniform and penetrating conversion coating on metallic surfaces using a zinc phosphate immersion process, thus overcoming the disadvantages inherent in the prior immersion processes and at the same time overcoming the disadvantages inherent in the prior spray processes.

In preparing zinc phosphate coatings suitable for application of rust preventive oil, attempts to apply such conversion coatings by immersion of the metal surfaces in a zinc phosphate bath have not produced optimal results due to the tendency under such conditions to form a coating which is coarse and granular and does

not provide an optimal base for rust preventive oil.

The present invention provides finer crystal structure and covers the metallic surface, including crevices, more completely, thereby providing greater rust protection than previously possible. The present invention also provides the capability of covering the areas of carbon residue found on steel surfaces.

The process of the present invention consists broadly of immersing a metallic surface in a conversion coating bath while exposing such immersed metallic surface to ultrasonic energy and while controlling the ultrasonic power environment to which the metallic surface is exposed.

We have discovered that when ultrasonic energy is applied to a metallic surface immersed in an aqueous zinc phosphate coating bath within a limited energy range, coating action is accelerated, resulting in fine-grained, uniform and smooth coatings superior to conversion coatings produced either by the immersion or by the spray processes of the prior art. The energy range may be limited by varying the energy produced by the transducers or by varying the positions of the transducers and metallic surface relative to each other curvilinearly so that the metallic surface passes through zones of varying energy intensities inherent to energy produced by ultrasonic transducers. The preferred frequency range for such ultrasonic energy lies in the range from about 18 kilohertz to about 60 kilohertz. Within this range there is no apparent optimum frequency but we have operated satisfactorily at 26 kilohertz, 40 kilohertz and 60 kilohertz.

We have also discovered that relative curvilinear motion between the metallic surface and the transducer during exposure to the ultrasonic energy produced fine-grained, uniform, smooth and unstriated coatings superior

to the conversion coatings produced by processes described in the prior art. The metallic surface was moved to and from the transducers in the tests by hand. In practice, the metallic surface may be moved by any of a number of mechanical means, such as the Pusher-Type Split-Rail Full Automatic plating machines sold by Occidental Metal Industries Corp., 21441 Hoover Road, Warren, Michigan 48089, the hoist method of Example XIV, or by tumbling the parts in a barrel as described in Example XIII. Under some conditions, benefits may be derived by moving the transducers with respect to the metallic surface or by placing transducers inside a metal cavity in order to coat an inside surface of a metal body. In other circumstances, it may be desirable to keep the transducers and metallic surface stationary relative to each other and to cause the metallic surface to pass through zones of varying energy intensities by varying the frequency of the ultrasonic energy.

It has also been discovered that with a high quality phosphate solution in conjunction with the application of ultrasonic power as detailed in this disclosure, areas of carbon residue inherently found on steel surfaces may be phosphate coated.

Finally, we have discovered that application of ultrasonic energy for only the first 15-30 seconds that the metallic surface is in the solution creates a plurality of nucleating sites sufficient to achieve the improved phosphate coating provided by the processes of this invention even where the phosphate coating process continues after the application of ultrasonic energy is discontinued.

The process of the present invention is applicable to applying conversion coatings to surfaces of steel, steel alloys, galvanized iron and aluminum and aliminum

alloys. Specific examples involving each of these metallic surfaces are set forth below. The examples below also demonstrate that, surprisingly, optimum results are obtained with the process of this invention only within a limited range of ultrasonic power. The power must be above the point of cavitation at the metal surface, but below a point at which the beneficial effects of the ultrasonic power diminishes. Although applicant does not wish to be bound to any particular theory of operation, the applicant believes that this upper limit is the point at which power above that point provides so much energy to the metal surface that the reaction cannot take place at the surface the product of the reaction cannot adhere to the surface.

As disclosed in the following examples, relative curvilinear motion between the metallic surface and the transducers during exposure to the ultrasonic energy produced fine-grained, uniform, smooth and unstriated coatings superior to the conversion coatings produced by processes described in the prior art. Curvilinear motion means motion which follows a curved path. Such curvilinear motion includes, but is not limited to, rotating and revolving, or any portion of a rotation or revolution. An example of partial revolution is the motion of the workpieces in the rotating drum of Example XIII. The axis of rotation or revolution may be horizontal, vertical or at any other angle. Also included in curvilinear motion is oscillating motion, such as the motion to and from the radiating surface in the first 12 examples below. Tumbling, twisting and turning is also contemplated in the definition of curvilinear motion. Sinusoidal movement is also included in the phrase curvilinear motion. Regardless of the type of curvilinear motion, an important characteristic is that at least a portion of the metallic

surface, for some period of time, moves toward or away from a plane containing the radiating surface of at least one of the ultrasonic transducers during exposure of the metallic surface to the ultrasonic energy. We believe that this type of motion moves the metallic surface through zones of varying energy intensities inherent to energy produced by ultrasonic transducers, thus avoiding the above-noted coating problems such as striation.

Example I

A rack of six 4"(W) x 6"(L) steel panels was first thoroughly cleaned with an alkali cleaner and then rinsed by dipping for one minute in a warm water rinse. An aqueous zinc phosphate conversion coating solution was then prepared containing the following ingredients in the amounts indicated:

Zinc as Zn	1.7 g/l
Phosphate as PO_4	5.5 g/l
Nitrate as NO_3	2.2 g/l
Nitrite as NO_2	0.1 g/l
Nickel as Ni	0.2 g/l
Magnesium as Mg	0.1 g/l
Fluoborate Ion	0.4 g/l

A solution of the above concentrations is prepared as follows. For each 100 gallons of solution, with the circulating pump running, add 15 fl. oz. of 50% sodium hydroxide. Allow the solution to circulate for 15 to 20 minutes and add 1 1/2 gallons of a solution containing the above ingredients to give the concentrations listed. Allow the resultant solution to again circulate for 15 to 20 minutes and check it for Free Acid Points (FAP) and Total Acid Points (TAP). FAP and TAP are discussed below. The TAP:FAP ratio should be 10:1 to 14:1, with a TAP of 9.0 to 12.0. Two to six fl. oz. of a nitrite accelerator to give the concentra-

tion given above are added 15 to 20 minutes prior to starting production. Both the solution containing the above ingredients to give the concentrations listed and the accelerator solution should be added continuously via proportioning pumps or dripping from a container. The accelerator level should be 2 to 4 ml.

To determine the FAP, place a 10 ml. sample of the bath in a clean beaker. Add one or two drops of methyl orange indicator solution. Titrate with 0.1 N sodium hydroxide until a straw-yellow color is obtained. The number of mls. of 0.1 N sodium hydroxide titrated is the FAP of the bath.

To determine the TAP, place a 10 ml. sample of the bath in a clean beaker. Add three to five drops of phenolphthalein indicator solution. Titrate with 0.1 N sodium hydroxide until a pink colour persists throughout the solution. The amount in ml. of 0.1 N sodium hydroxide titrated is the TAP of the bath.

To measure the accelerator level, place a 25 ml. sample of the bath in a clean beaker. Add 10 to 15 drops of 50% sulfuric acid to the sample. Titrate with 0.042 N potassium permanganate until a purplish color persists for 20 to 30 seconds but fades out within 60 seconds. The amount in mls. of 0.042 N potassium permanganate titrated is the accelerator level of the bath.

Sixty-four gallons of the above aqueous solution were put into a stainless steel container measuring 2 feet square and 2 feet deep. The top of the solution was 1 inch from the top of the container. Within such container and attached to the bottom thereof were two stainless steel containers containing 9 lead zirconate titanate transducers adapted to being connected to an external power supply. The distance from the top of the transducer containers to the top of the solution was

18 inches. Each transducer container was rated at 350 watts at full power with the power input being variable. The transducers were operated at full power for 30 minutes with the solution at 140°F in order to degas the aqueous zinc phosphate coating solution. The power input to the transducers was then reduced to below the cavitation point and a rack containing six of the previously cleaned steel panels was lowered into the coating solution to a depth wherein the top edges of the panels were 1 inch below the top of the solution. Power input was increased to just above the cavitation point and maintained for a period of two minutes at that power level with the bath at 140°F.

The steel panels were painted and salt spray tested. These tests showed that panels produced by the process of this example were highly superior in performance to panels produced by the previous conventional procedures.

Example II

The steps of Example I were repeated several times at progressively higher power levels until the onset of formation of an irregular, nonuniform coating was observed. The results indicated that smooth, uniform coatings were formed as the power levels were raised about 1.32 Watts/gal. of solution and 0.20 Watts/square inch radiating surface until at 7.94 Watts/gal. of solution and 1.16 Watts/sq. in. radiating surface the onset of the formation of an irregular, nonuniform coating was observed. The onset of formation of an irregular nonuniform coating is the point at which the beneficial effects of the ultrasonic energy diminishes. Thus the improved results of the present invention were obtained in this case in the range from 1.32 Watts/gal. of solution and 0.20 Watts/sq. in. radiating surface to just below 7.94 Watts/gal. of solution and 1.16 Watts/sq.

in. radiating surface. The coating values obtained at the progressively higher power levels were as follows:

Watts/gal. of Solution	Watts/sq.in. Radiating Surface	Coating Weight	Nature of Coating
1.32	0.20	120mg/sq.ft	Regular, uniform
1.76	0.26	170mg/sq.ft	" "
2.67	0.39	230mg/sq.ft	" "
4.41	0.65	220mg/sq.ft	" "
7.94	1.16	200mg/sq.ft	Irregular, nonuniform
10.29	1.51	160mg/sq.ft	Irregular, nonuniform

The steel panels were painted and salt spray tested. These tests showed that panels produced by the optimum range of the process of this example were highly superior in performance to panels produced by the previous conventional procedures.

Example III

The process of Example I was carried out using panels made from Aluminum alloy 2024. The test procedure of Example II was then followed and the following results were obtained:

Watts/gal. of Solution	Watts/sq.in. Radiating Surface	Coating Weight	Nature of Coating
1.32	0.20	195mg/sq.ft	Smooth, uniform fine crystals
2.67	0.39	282mg/sq.ft	Smooth, uniform fine crystals
10.29	1.51	160mg/sq.ft	Irregular, nonuniform fine crystals

The aluminum panels were salt spray tested. These tests showed that panels produced by the optimum range of the process of this example were highly superior in performance to panels produced by the previous conven

tional procedures.

Example IV

The process of Example I was carried out using galvanized iron panels in place of the steel panels of Example I. The test procedure of Example II was followed for values of no power and of 2.67 Watts/gal. of solution and 0.39 Watts/sq. in. radiating surface.

Watts/gal. of Solution	Watts/sq.in. Radiating Surface	Nature of Coating
0	0	Irregular, nonuniform, coarse crystals,
2.67	0.39	Regular, uniform, fine crystals,

The galvanized iron panels were painted and salt spray tested. These tests showed that panels produced by the process of this example were highly superior in performance to panels produced by the previous conventional procedures.

Example V

The process of Example I was carried out using an aqueous zinc phosphate conversion coating solution containing the following ingredients in the amounts indicated:

Zinc as Zn	2.5 g/l
Phosphate as PO^4	6.6 g/l
Nitrate as NO_3	2.0 g/l
Nitrite as NO_2	0.1 g/l
Fluosilicic Ion	0.4 g/l

A solution of the above concentrations is prepared as follows. For each 100 gallons of solution, add to the heated (120°F) water, with circulating pump running, the following materials in the sequence listed.

(a) One pound of Caustic (dissolved in water).

(b) One and one-half gallons of solution containing the above ingredients to give the

concentration listed.

(c) Six to eight fl. oz. of solution prepared by dissolving two pounds of sodium nitrite material per gallon of water.

The FAP should be 0.8 to 1.2, while the TAP should be 10 to 16 and the accelerator level one to four ml. The operating temperature of the bath should be between 120°F and 150°F. The FAP, TAP and accelerator level were determined as in Example I.

The steel panels were painted and salt spray tested. The results of these tests were substantially the same as in Example I.

Example VI

The process of Example I was carried out using an aqueous zinc phosphate conversion coating solution containing the following ingredients in the amounts indicated:

Zinc as Zn	1.8 g/l
Phosphate as PO_4	8.0 g/l
Nitrate as NO_3	17.0 g/l
Nitrite as NO_2	0.1 g/l
Nickel as Ni	0.2 g/l
Magnesium as Mg	0.3 g/l
Calcium as Ca	5.2 g/l
Fluosilicic Ion	5.0 g/l

A solution of the above conventrations is prepared as follows. For each 100 gallons of solutions, add the following material to the circulating water:

(a) 1.2 gallons of solution containing all of the ingredients listed except calcium and nitrite.

(b) 3 gallons of Additive solution containing ingredients to give the concentration of calcium listed.

(c) 5 ounces of Caustic dissolved in water or

190 ml. of 50% Caustic.

(d) 13 fl. oz. of Activator solution containing nitrite added twenty minutes prior to starting production.

The FAP should be 0.7 to 0.9, while the TAP should be 12 to 15 and the Activator 1.5 to 2.3. The operating temperature of the bath should be between 145°F and 155°F. The FAP and TAP were determined as in Example I.

The steel panels were painted and salt spray tested. The results of these tests were substantially the same as in Example I.

Example VII

Three 4"(W) x 12"(L) steel panels, A, B and C were first thoroughly cleaned with an alkali cleaner and then rinsed by dipping for 30 seconds in cold water. Fifty gallons of an aqueous zinc phosphate conversion coating solution at 150°F were prepared as described in Example I and put into a stainless steel container measuring two feet square. The top of the solution was 23 inches above two ultrasonic transducer containers of the type described in Example I. The three steel panels, A, B and C, were placed in the solution for two minutes. Steel panel A was held one inch below the surface of the solution with no ultrasonic agitation or panel movement. Steel panel B was held stationary one inch below the surface of the solution with the two ultrasonic transducer containers operating at full power. Steel panel C was placed in the solution with the two ultrasonic transducer containers operating at full power and moved up and down from one inch below the top of the solution to two inches from the bottom at a rate of 20 cycles per minute for two minutes. The steel panels were then rinsed by a 30 second dip in cold water followed by a passivating rinse. The following results were obtained:

Test Panel	Visual Appearance	Crystal Size	Coating Weight mg/ft²
A (No sonic energy or panel movement)	Smooth coating	Coarse	473
B (Sonic energy and no panel movement)	Irregular coating	Much finer than Panel A	384
C (Sonic energy and panel movement)	Smooth coating	Much finer than Panel A	347

Example VIII

The process of Example VII was repeated except that galvanized steel panels were used instead of steel panels. The following results were obtained:

Test Panel	Visual Appearance	Crystal Size	Coating Weight mg/ft²
A (No sonic energy or panel movement)	Smooth coating	Coarse	653
B (Sonic energy and no panel movement)	Irregular coating	Much finer than Panel A	726
C (Sonic energy and panel movement)	Smooth coating	Much finer than Panel A	675

Example IX

The process of Example VII was repeated except that the panels were immersed for five minutes and a zinc phosphating solution suitable for producing a heavy coating which serves as a base for rust preventive oil was used. The solution contains the following ingredients in the amounts indicated:

Zinc as Zn	7.5 g/l
Phosphate as PO_4	19.8 g/l

Nitrate as NO_3 6.0 g/l

A solution of the above concentration is prepared as follows. For each 100 gallons of solution, add to heated (125°F) water, 3 1/2 gallons of solution containing the foregoing ingredients to give the concentrations listed. The FAP should be 5 to 7, while the TAP should be 30 to 35. The operating temperature of the bath should be 185°F to 205°F. The FAP and TAP were determined as in Example I.

The following results were obtained:

Test Panel	Visual Appearance	Crystal Size	Coating Weight mg/ft^2
A (No sonic energy or panel movement)	Smooth coating	Coarse	1,176
B (Sonic energy and no panel movement)	Irregular coating	Much finer than Panel A	1,287
C (Sonic energy and panel movement)	Smooth coating	Much finer than Panel A	1,329

Example X

The process of Example IX was repeated except that ten test panels, numbered 2-11, were immersed for various lengths of time, test panels 2, 3, 4 and 5 were exposed to no ultrasonic energy and the ultrasonic energy was applied to test panels 10 and 11 for a limited time and then stopped while the reaction proceeded. The following results for the various test conditions were obtained:

Test Panel No.	Total Length of Time Immersed	Length of Time Ultrasonic Energy Was Applied	Coating Weight mg/ft^2	Appearance
2	15 sec.	0	186	Coarse coating
3	1 min.	0	853	Coarse coating
4	2 min.	0	1,201	Coarse coating
5	5 min.	0	1,248	Coarse coating
6	15 sec.	15 sec.	241	Finer coating than Panel 2
7	1 min.	1 min.	958	Finer coating than Panel 3
8	2 min.	2 min.	1,252	Finer coating than Panel 4
9	5 min.	5 min.	1,332	Finer coating than Panel 5
10	2 min.	First 15 sec.	1,250	Fine coating-finer than Panel 4 but coarser than Panel 8
11	2 min.	First 30 sec.	1,188	Fine coating-similar to Panel 10

Example XI

Twelve 4"(W) x 12"(L) steel panels were first thoroughly cleaned with an alkali cleaner and then rinsed by dipping for one minute in a warm water rinse. An aqueous zinc phosphate conversion coating solution was then prepared as in Example IX.

Sixty-four gallons of the aqueous solution were put into a stainless steel container measuring two feet square and two feet deep. Within the container and attached to the bottom thereof were two stainless steel containers containing piezoelectric type transducers generating 26.5 kilocycles per second. Each of the two containers was rated at 350 watts of full power with the power input being variable. The distance from the top of the transducer containers to the top of the solution was 18 inches. The steel panels were placed one inch below the surface of the solution at various power settings and held stationary in the solution for various lengths of time as shown in the table below. The steel panels were then rinsed by two one-minute dips in cold water and a passivating rinse. Next, the steel panels were oiled by a five-minute dip in rust preventive oil and salt spray tested. The results are presented in the table below:

Watts/gal. of solution	Watts/sq.in. Radiating Surface	Phos.Time: 5min.	15min.	5min.	15min.
0 (Control)	0	2300	2650	24	64
0.75	0.11	2150*	2250*	64	88
1.63	0.24	2200*	2250*	64	112
2.52	0.37	1350*	1300*	64	136
4.41	0.65	1350*	1350*	236	236
8.64	1.27	1400*	1350*	320	320

Phos. Time is the length of time the test panel was held in solution.
*Coatings noted by * have smooth regular coating. All other coatings have lighter color, are not as smooth and have much coarser coatings. The coatings at 2.52W/gal. and 0.37 W/sq.in, 4.41 W/gal. and 0.65 W/sq.in. and 8.64 W/gal. and 1.27 W/sq.in. have particularly fine crystal size.

Example XII

The process of Example XI was followed except that the solution contained the following ingredients in the amounts indicated:

Zinc as Zn	7.2 g/l
Phosphate as PO_4	19.1 g/l
Nitrate as NO_3	5.7 g/l
Cobalt as CO	0.03 g/l

A solution of the above concentrations is prepared as follows. For each 100 gallons of solution, add to heated (120°F) water, 4 gallons of solution containing the foregoing ingredients to give the concentrations listed. The FAP should be 5 to 7, while the TAP should be 30 to 35. The operating temperature of the bath should be 185°F to 205°F. The FAP and TAP were determined as in Example I.

The following results were obtained:

Watts/gal. of Solution	Watts/sq.in. Radiating Surface	COATING WEIGHT MG/FT²		OILED SALT SPRAY HRS. BEFORE RUST	
Phos.Time:		5min.	15min.	5min.	15min.
0 (Control)	0	2870	3200	24	64
0.75	0.11	2700*	3150*	48	112
2.52	0.37	2050*	2250*	136	150
4.41	0.65	2250*	1900*	480	480
8.64	1.27	2250*	1800*	480	480

Phos. Time is the length of time the test panel was held in solution

*Coatings noted by * have smooth regular coating. All other coatings have lighter color, are not as smooth and have much coarser coatings. The coatings at 2.52 W/gal. and 0.37 W/sq.in., 4.41 W/gal. and 0.65 W/sq.in., and 8.64 W/gal. and 1.27 W/sq.in. have particularly fine crystal size.

Example XIII

Fig. 21 shows a plurality of ultrasonic transducers 51 arranged in a harness 55. Ultrasonic transducers 51 are held in place by metal sheets 52 attached to harness 55. Harness 55 with ultrasonic transducers 51 was placed in a phosphate conversion coating bath 61 as shown in Fig. 22. Harness 55 is equipped with support arms 53 which support harness 55 in conversion coating bath 61 by resting on the top edges 62 of the tank holding the conversion coating bath 61. Perforated drum 70 is supported by arms 71 connected to axle 72. Arms 71 are attached to frame 73, which may be raised or lowered by a mechanism, not shown in the figures, positioned above frame 73. Although the mechanism for raising and lowering frame 73 is not shown, any of a number of well known mechanisms, such as the Programat Bulk Processing Machines or the H.O.B. Programat Hoist System sold by Occidental Metal Industries Corp., mentioned above, may be used. Attached to frame 73, is a motor 74, shown in Fig. 23. Motor 74 drives gear 76 by means of gear 75. Gear 76 is securely fastened to drive shaft 77, which drives bull gear 79 by means of gear 78. Bull gear 79 is securely attached to drum 70, so that motor 74 causes drum 70 to rotate by means of the mechanism described above. Drums such as described above include Udy-Pro Gear-Driven Polypropylene Plating Barrels and Heavy-Duty Gear-Driven Tumbling Barrels by Occidental Metal Industries Corp., noted above.

Several metallic pieces were placed in drum 70. Drum 70 was lowered into frame 55 which was suspended in the conversion coating bath, as shown in Fig. 22. The perforations in drum 70 allowed the bath to flow through the drum. Motor 74 and ultrasonic transducers 51 were activated. The optimum power level of the ultrasonic

transducers -- a level above cavitation, but below the limit at which the beneficial effects of ultrasonic power substantially diminished -- was determined in a limited number of tests.

The conversion coatings produced on the metallic surfaces by this process were superior to those produced by processes of the prior art.

Example XIV

An automobile body may be attached to a platform which may be rotated in any of a number of ways. For example, the drum in Example XIII may be replaced with a platform positioned on the axle described in Example XIII. If desired, the bull gear may be replaced with a smaller gear and a belt that connects the smaller gear to the drive shaft. The automobile body may be lowered into a phosphate conversion coating bath and partially surrounded by ultrasonic transducers as was the drum in Example XIII. The automobile may then be revolved about the axle attached to the platform while ultrasonic energy is applied.

BRIEF DESCRIPTION OF THE DRAWINGS

The annexed Figures 1 to 10 consist of photo-lithographic reproductions of photomicrographs of various metallic surfaces formed in the practice of the present invention taken with an electron microscope at various magnifications. These figures show the conversion coating crystal formations as follows:

Figure 1 is a photomicrograph of a panel from Example I with no ultrasonic power applied at manifi-cation 375X;

Figure 2 is a photocicrograph of a panel from Example I with ultrasonic power applied at 2.67 Watts/gal. of solution and 0.39 Watts/sq.in. radiating surface at magnification 375X;

Figure 3 is the same as Fig. 1 but at magnification 1500X;

Figure 4 is the same as in Fig. 2 but at magnification 1500X;

Figure 5 is the same as Fig. 1 with immersion time of five minutes instead of two minutes;

Figure 6 is the same as Fig. 2 with immersion time of five minutes instead of two minutes;

Figure 7 is the same as Fig. 5 but at magnification 1500X;

Figure 8 is the same as Fig. 6 but at magnification 1500X;

Figure 9 is a photomicrograph of a panel from Example IV with no ultrasonic power applied at magnification 300X.

Figure 10 is a photomicrograph of a panel from Example IV with ultrasonic power applied at 2.67 Watts/gal. of solution and 0.39 Watts/sq.in. radiating surface at magnification 300X;

Figure 11 is a scanning electron photomicrograph of a typical steel surface;

Figure 12 is a carbon dot map of the steel surface in Figure 11;

Figure 13 is a scanning electron photomicrograph of a steel surface coated by a method of the prior art;

Figure 14 is a carbon dot map of the steel surface of Figure 13;

Figure 15 is an X-Ray spectrographic analysis of the steel surface of Figure 13;

Figure 16 is a scanning electron photomicrograph superimposed by an X-Ray spectrographic analysis of a steel surface;

Figure 17 is a carbon dot map of the steel surface of Figure 16;

Figure 18 is a scanning electron photomicrograph of a steel surface coated by a method of the present invention;

Figure 19 is a zinc dot map of the steel surface of Figure 18;

Figure 20 is an iron dot map of the steel surface of Figure 18;

Figure 21 is a perspective view of a harness containing ultrasonic transducers;

Figure 22 is a side view of a rotating drum assembly within a harness containing ultrasonic transducers and submerged in a phosphate coating bath; and

Figure 23 is a local transverse vertical cross-sectional view taken substantially on the line 23-23 of Figure 22.

DETAILED DESCRIPTION OF THE DRAWINGS

The greatly improved results obtained in the practice of the present invention are clearly apparent in the drawings. For instance, in Figure 1 there are widely scattered relatively large needle like crystals typical of the irregular nonuniform coatings produced by the prior art immersion processes, whereas in Figure 2 the crystals formed using the process of the present invention are much finer and more numerous. These differences are further evident in Figures 3 and 4 at much higher magnification. Also at the higher magnifications of Figures 3 and 4 it is apparent that the metallic surface is completely covered by crystals in Figure 4 as compared to incomplete coverage in Figure 3. These differences are also present in Figures 5 and 6 where the immersion was for a longer time period (five minutes as compared to two minutes for Figures 1 and 2) and are even more apparent at the higher magnifications of Figures 7 and 8.

In Figure 9, which illustrates the results obtained on galvanized iron in the prior art immersion process, relatively coarse and discontinuous crystals are shown as compared with the smooth, continuous crystal

formation shown on a galvanized iron panel treated in accordance with the process of the present invention.

In describing the process of the present invention we have referred to specific conversion coating formulations which are particularly adapted to forming coatings which are satisfactory for later applications of siccative coatings such as paint. However, it is important to note that the present invention is not limited to the use of these particular formulations since other zinc phosphate coating formulations may be used to achieve substantially similar improved results for the same purpose. While the precise mechanisms involved in the application of ultrasonic energy to metallic surfaces immersed in zinc phosphate conversion coating baths are not known, it is the application of such ultrasonic energy in controlled ultrasonic power environments which is significant rather than the particular constitution of the zinc phosphate conversion coating baths. Apparently the application of ultrasonic energy within a controlled ultrasonic power environment to a metallic surface immersed in a zinc phosphate conversion bath has an effect on crystal formation which, surprisingly, leads to smooth, uniform coatings rather than the expected irregular, nonuniform coatings.

Figure 11 is a scanning electron micrograph of a typical steel surface. A surface analysis of the steel surface in Fig. 11 is displayed as the carbon dot map of Figure 12. The lighter areas of the carbon dot map are areas of high carbon concentration. These figures show that what appear to be raised areas on the metal surface in Figure 11 are actually the areas of high carbon residue which is inherently found on steel surfaces.

Figure 13 is a scanning electron photomicrograph of

a steel surface coated by a method of the prior art. The photomicrograph shows an area of steel left uncovered by crystals. A surface analysis of this steel surface presented by the carbon dot map of Figure 14, shows that the uncoated area of the steel surface in Figure 13 is an area of carbon residue. A wavelength analysis, Figure 15, shows that the coating on the steel surface shown in Figure 13 is a poor zinc phosphate coating.

The scanning electron photomicrograph superimposed by an X-Ray spectrographic analysis, Figure 16, shows a high quality calcium zinc phosphate coating, 210 mg/ft, on a steel surface. A wavelength analysis of the carbon distribution on the steel surface of Figure 16, is displayed as the carbon dot map, Figure 17, wherein the lighter areas are areas of high carbon concentration. Figures 16 and 17 show that even the areas of high carbon residue concentration on the steel surface of Figures 16 and 17 were coated by high quality calcium zinc phosphate crystals.

Figure 18 is a scanning electron photomicrograph of a steel surface coated by a method of the present invention. Figure 18 bears a high quality coating. Figures 19 and 20 are surface analyses of the surface shown in Figure 18. Figure 19 is a zinc dot map which shows the areas of high zinc concentration. The lighter areas of Figure 19 are areas of higher zinc concentration. Figure 20 is an iron dot map of the surface shown in Figure 18. The lighter areas of Figure 20 are areas of higher iron concentration. Figures 18, 19 and 20 show that problem steel, i.e. steel which inherently contains areas of high carbon residue concentration, may be coated by a process of the present invention with a phosphophyllite solution, $Fe\ Zn(PO_4)$, to give a high quality generally uniform coating. Figures 16 and 17

showed the uniform coating could be achieved by a method of this invention utilizing a scholzite solution containing calcium zinc phosphate, $Ca\ Zn(PO_4)$.

Claims:

1. A process for forming improved zinc phosphate conversion coatings on metallic surfaces comprising the steps of:

a) immersing the metallic surface to be coated in a zinc phosphate conversion coating bath;

b) exposing the immersed metallic surface to ultrasonic energy during at least part of the conversion coating process, said ultrasonic energy produced by means of at least one ultrasonic transducer submerged within the zinc phosphate coating bath;

c) moving said immersed metallic surface curvilinearly with respect to said transducers during at least part of the exposure to ultrasonic energy; and

d) controlling the ultrasonic energy produced by such ultrasonic transducers so that the ultrasonic energy impinging on the metallic surface is above the point of cavitation and below a point at which the beneficial effects of the ultrasonic energy substantially diminishes.

2. A process for forming improved zinc phosphate conversion coatings on metallic surfaces comprising the steps of:

a) immersing the metallic surface to be coated in a zinc phosphate conversion coating bath;

b) exposing the immersed metallic surface to ultrasonic energy during at least part of the conversion coating process, said ultrasonic energy produced by means of a plurality of ultrasonic transducers submerged within the zinc phosphate coating bath and arranged at least partially around said immersed metallic surface during at least part of the conversion coating process;

c) moving said immersed metallic surface curvilinearly with respect to said transducers during at least part of the exposure to ultrasonic energy; and

d) controlling the ultrasonic energy produced by such ultrasonic transducers so that the ultrasonic energy impinging on the metallic surface is above the point of cavitation and below a point at which the beneficial effects of the ultrasonic energy substantially diminishes.

3. The process of claim 1 in which the metallic surface is steel or an alloy of steel.

4. The process of claim 1 in which the metallic surface is galvanized iron.

5. The process of claim 1 in which the metallic surface is aluminum or an alloy of aluminum.

6. The process of claim 1 in which the frequency of the ultrasonic energy lies above about 18 kilohertz.

7. The process of claim 1 in which the frequency of the ultrasonic energy lies in the range from about 18 kilohertz to about 60 kilohertz.

8. The process of claim 1 further comprising the step of oiling the exposed metallic surface with a rust preventive oil.

9. The process of claim 1 further comprising the step of painting the exposed metallic surface.

10. The process of claim 1 in which such ultrasonic transducers inherently produce varying zones of energy intensities within said conversion coating bath, and further comprising the step of repeatedly varying the positions of said immersed metallic surface and such ultrasonic transducers relative to each other whereby said immersed metallic surface passes repeatedly through said varying zones of energy intensities.

11. The process of claim 10 in which the positions of said immersed metallic surface and such ultrasonic transducers relative to each other are varied whereby said immersed metallic surface passes repeatedly through said varying zones of energy intensities by moving said immersed metallic surface repeatedly through said varying

zones of energy while such ultrasonic transducers are maintained in a stationary position.

12. The process of claim 10 in which the positions of said immersed metallic surface and such ultrasonic transducers relative to each other are varied whereby said immersed metallic surface passes repeatedly through said varying zones of energy intensities by maintaining said immersed metallic surface in a stationary position and moving such ultrasonic transducers repeatedly such that said zones of varying energy intensities repeatedly pass over said immersed metallic surface.

13. The process of claim 10 in which the positions of said immersed metallic surface and such ultrasonic transducers relative to each other are varied whereby said immersed metallic surface passes repeatedly through said varying zones of energy intensities by moving said immersed metallic surface and such ultrasonic transducers repeatedly such that said immersed metallic surface passes through said zones of varying energy intensities.

14. The process of claim 1 in which the improved zinc phosphate conversion coatings are formed on metallic surfaces by exposing said immersed metallic surface to ultrasonic energy for a limited time and retaining said immersed metallic surface immersed in said conversion coating bath for a further limited time while the conversion coating reaction proceeds.

15. A metallic surface having adherently attached thereto a smooth, uniform conversion coating applied by means of the process of claim 1.

16. A metallic surface having adherently attached thereto a smooth, uniform conversion coating applied by means of the process of claim 3.

17. A metallic surface having adherently attached

thereto a smooth, uniform conversion coating applied by means of the process of claim 4.

18. A metallic surface having adherently attached thereto a smooth, uniform conversion coating applied by means of the process of claim 5.

19. A metallic surface having adherently attached thereto a smooth, uniform conversion coating and rust preventive oil applied by means of the process of claim 8.

20. A metallic surface having adherently attached thereto a smooth, uniform conversion coating and paint applied by means of the process of claim 9.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

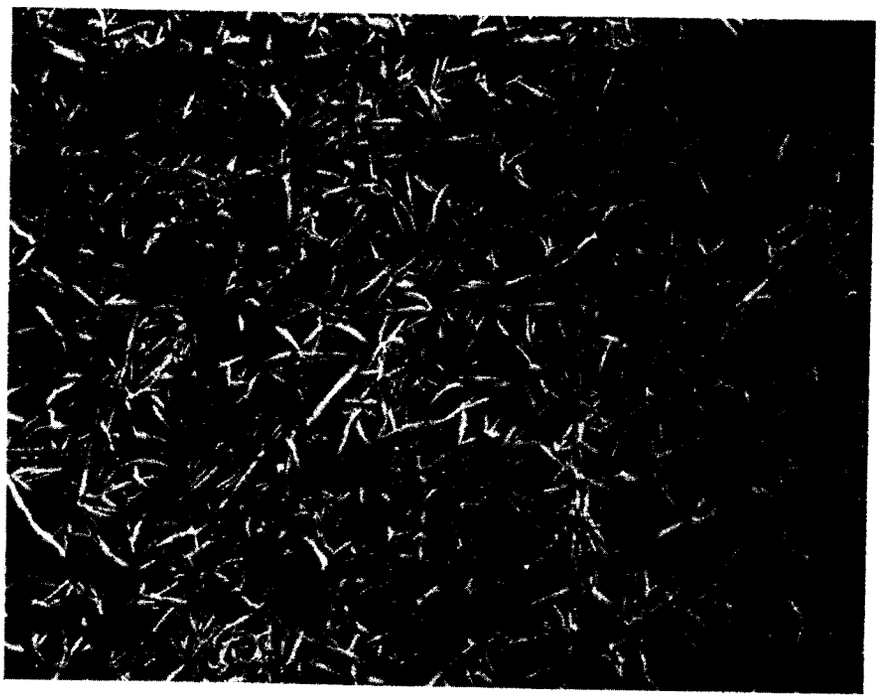

Fig. 6

Fig. 7

Fig. 8

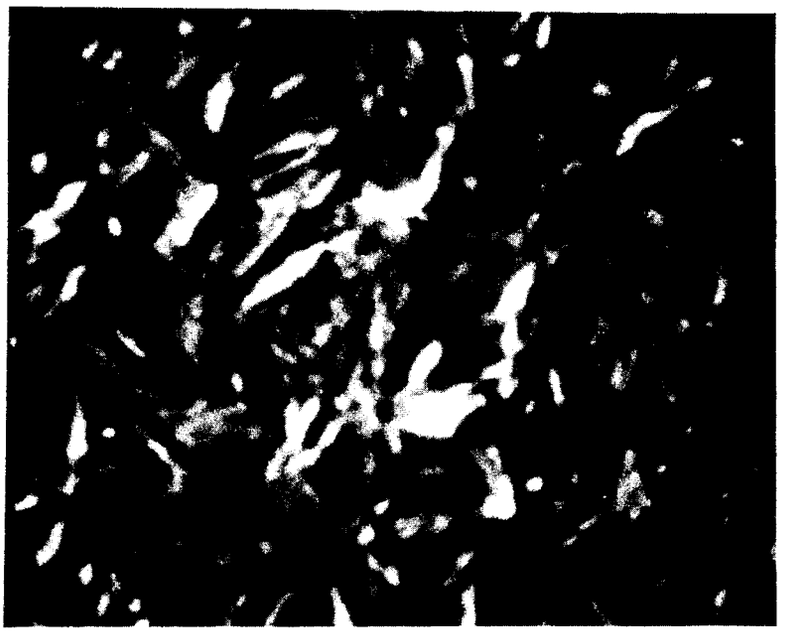

Fig. 9

Fig. 10

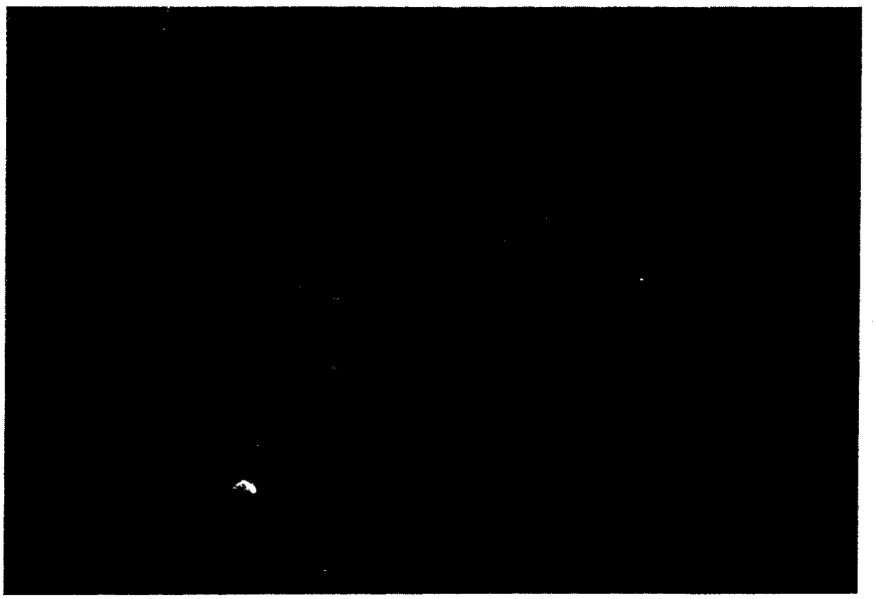

FIG.11

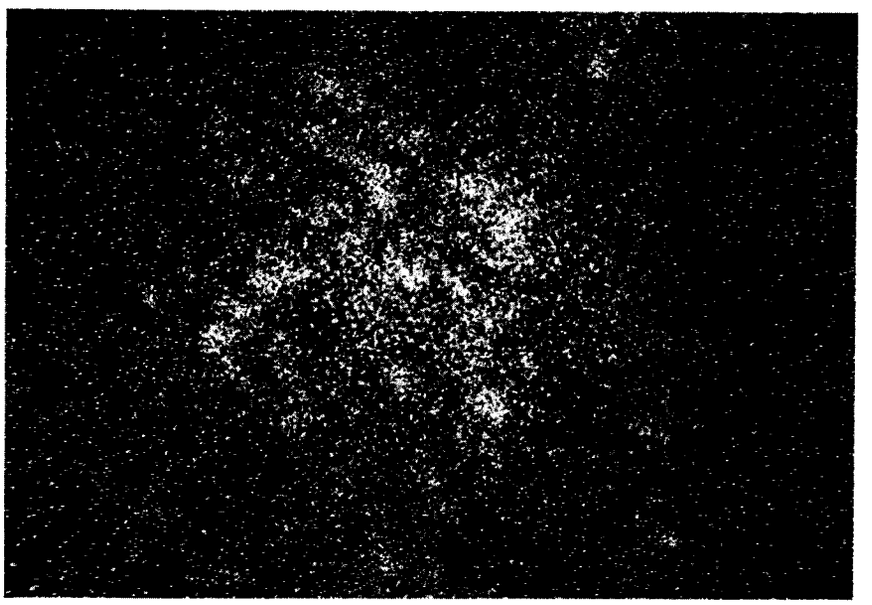

FIG.12

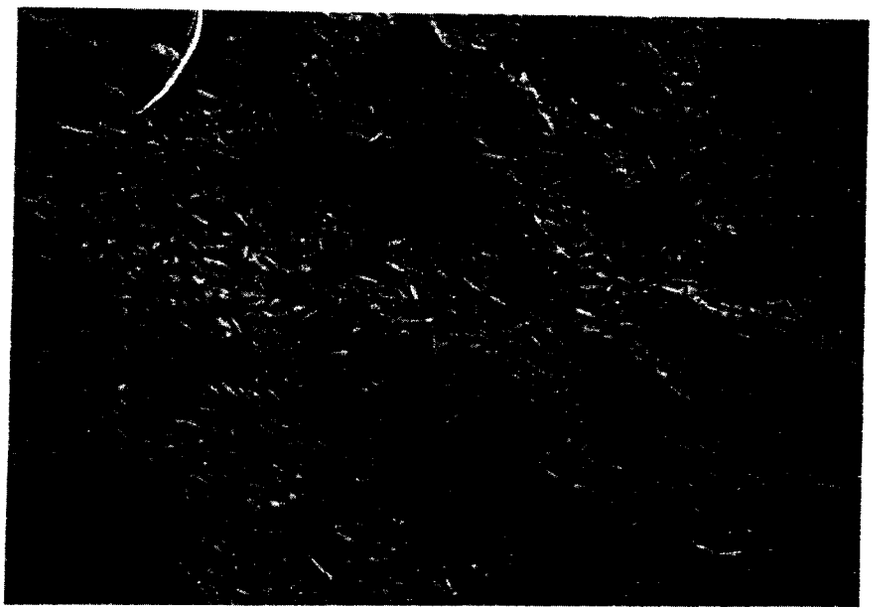

FIG. 13

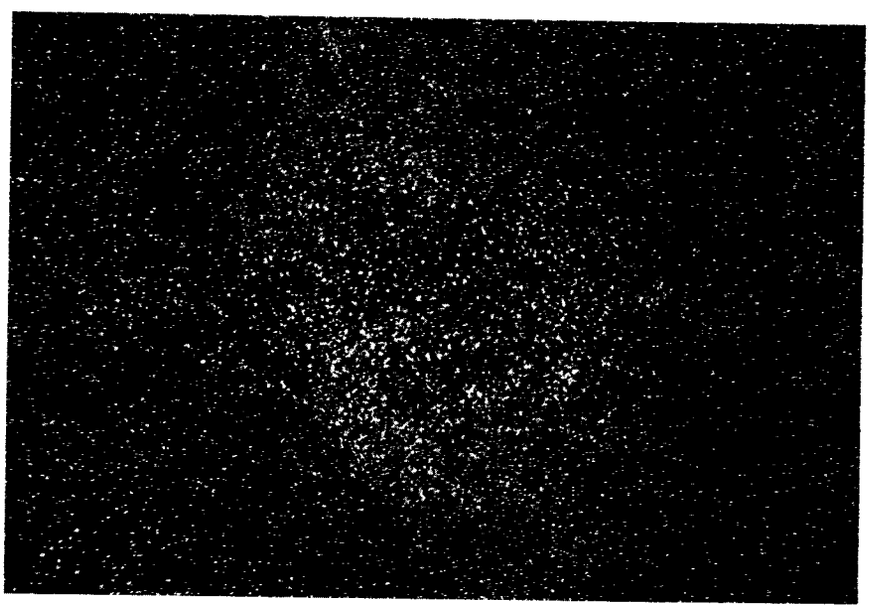

FIG. 14

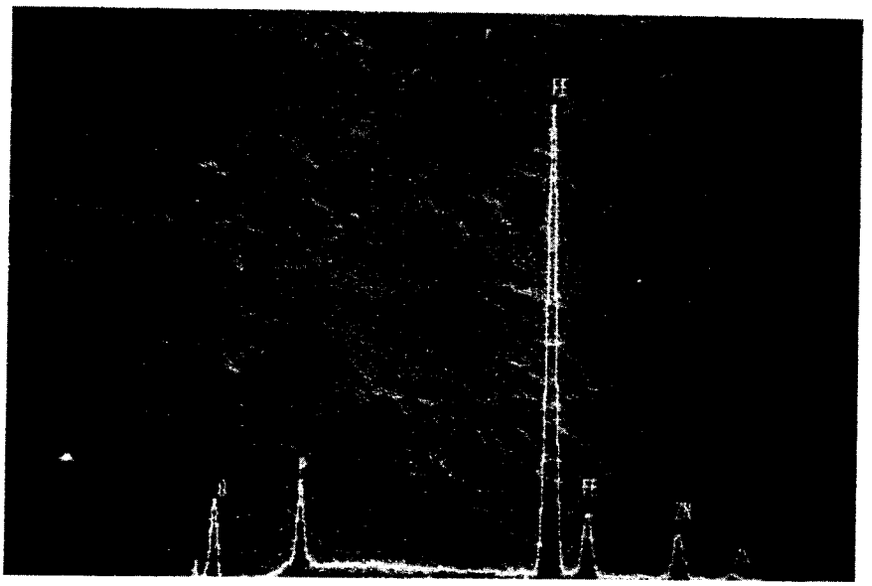

FIG. 15

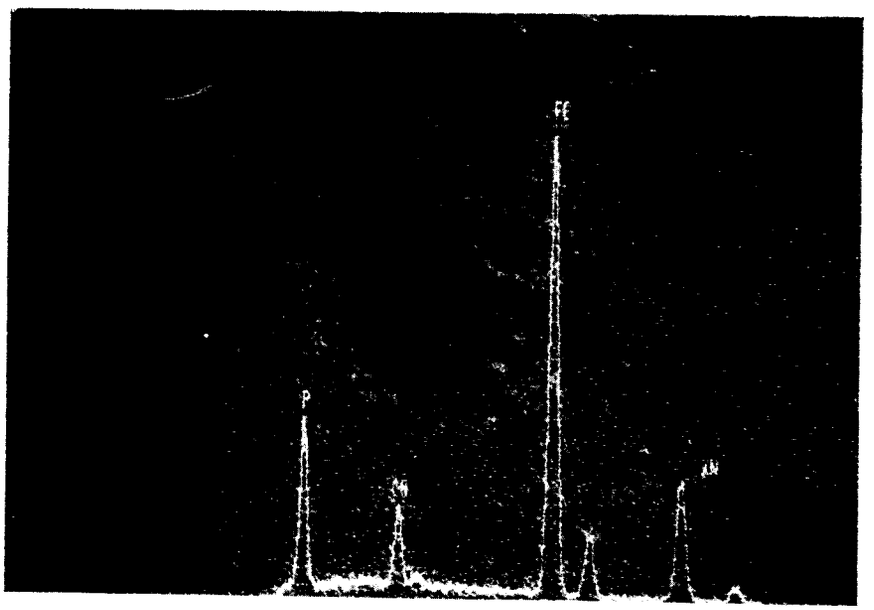

FIG. 16

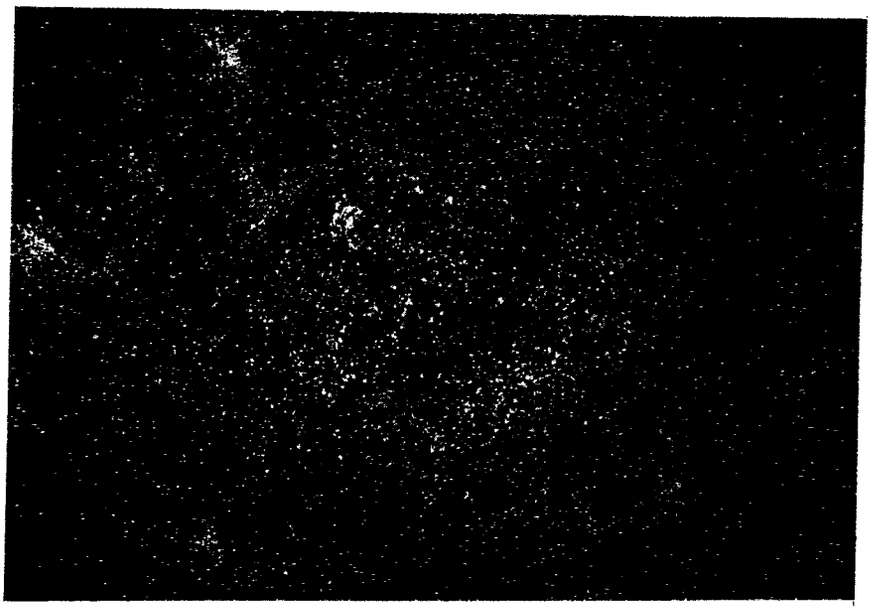

FIG. 17

FIG. 18

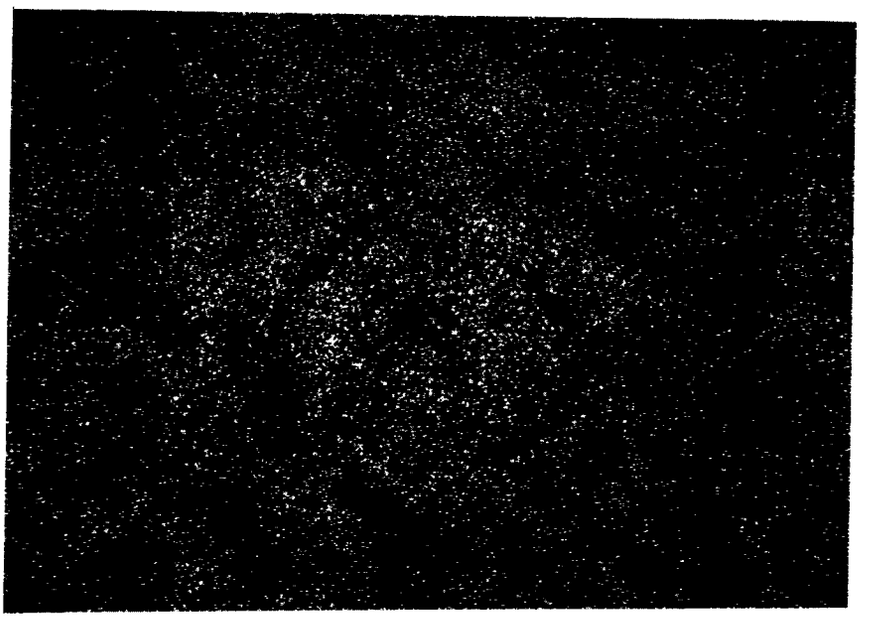

FIG. 19

FIG. 20

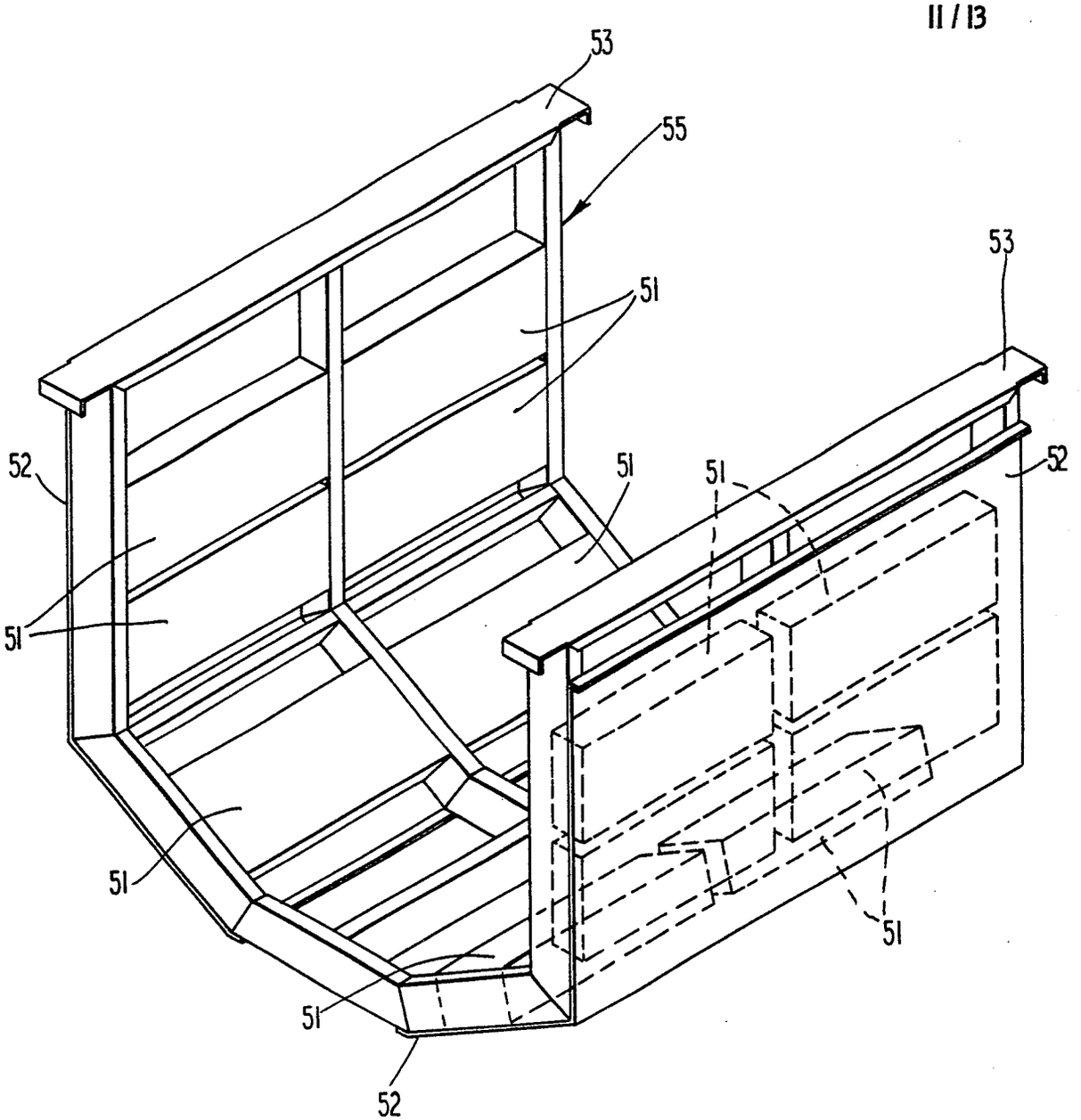

Fig. 21

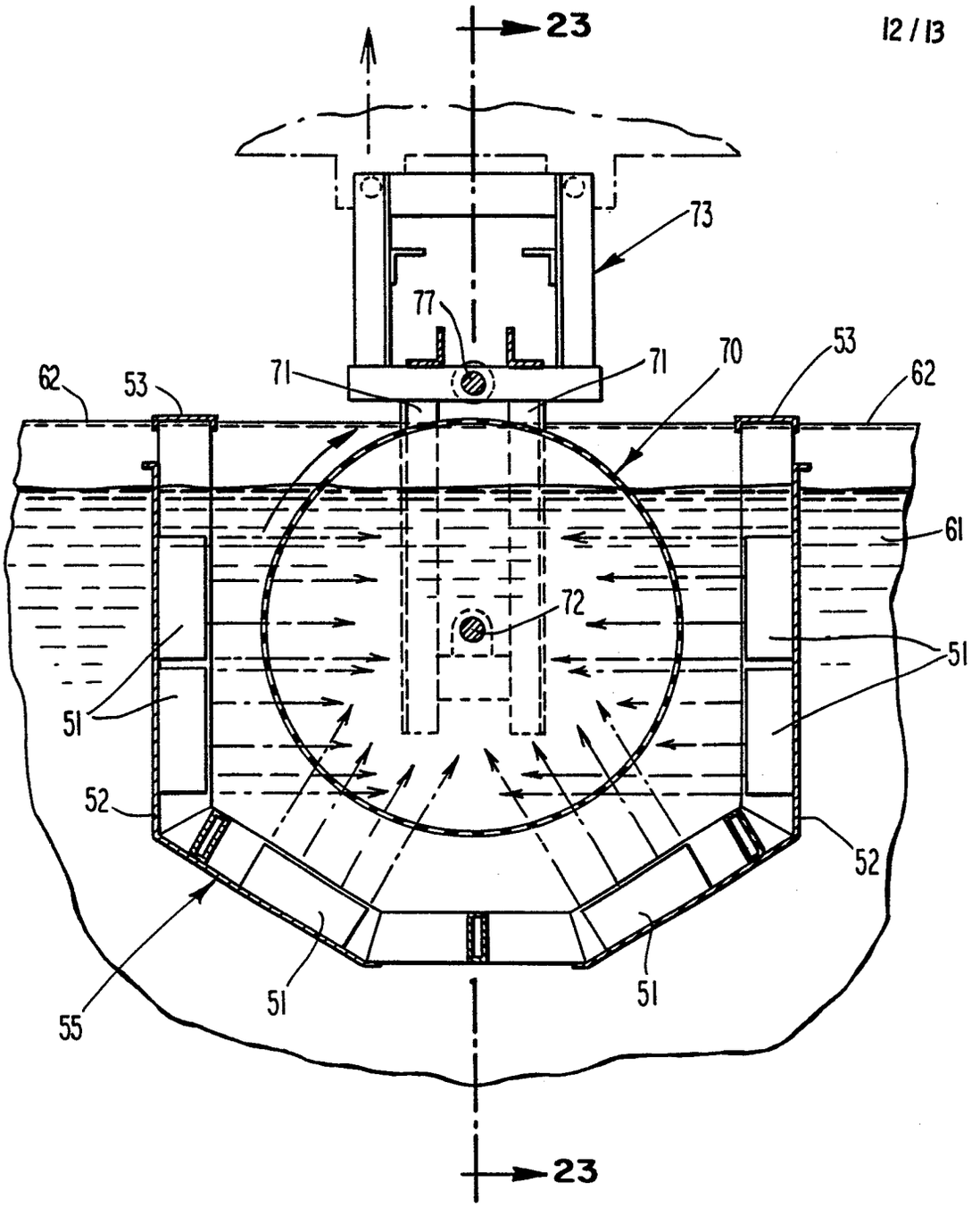

Fig. 22

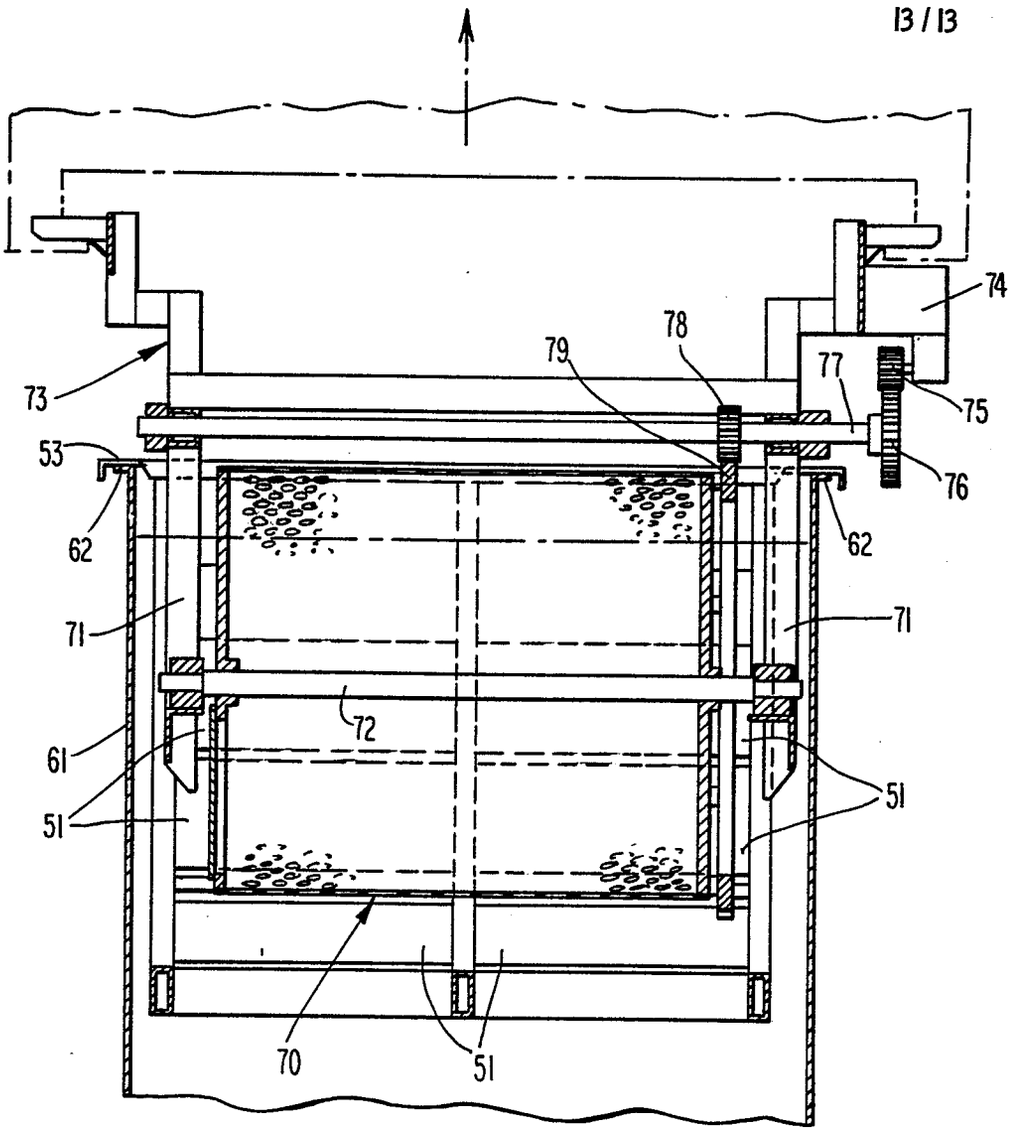

Fig. 23

0114087

European Patent Office

EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 84300015.9

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	GB - A - 1 588 912 (CAMPAGNIA CONTINENTALE S.C.E.A.R., S.R.L.) * Totality, especially page 1, lines 17-22, lines 69-90; page 2, lines 6-17; fig. 1; claims *	1-20	C 23 F 7/08 C 23 F 7/10 C 23 F 7/14 B 01 J 19/10
A	US - A - 4 287 004 (R. MURAKAMI et al.) * Fig.; claims *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 23 F
B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	22-03-1984	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503. 03.82